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Summary of Accomplishments

An improved molecular level understanding of the fundamental relationship between molecular properties and macroscopic properties of highly viscous liquids and sol-gel prepared glasses represented the main goal of research supported by this grant. In addition, the behavior of fluids in confined geometries was investigated. Further development of unique NMR and laser Raman scattering instrumentation for experiments under extreme conditions of high pressure continued to represent an important part of our research.

In the project dealing with liquids confined to porous glasses, we succeeded, for the first time, to investigate the effect of pressure on the dynamics of liquids confined to porous glasses, and also to record a high-resolution NMR spectrum of a model lubricant in confined geometries. These unique experiments not only open new directions in the research on liquids in confined geometries but have important implications for the applied field of lubrication.

1. Unique Character of Our Research Effort

There are several specific aspects of our work which make our research efforts unique. First, about 22 years ago we started our measurements on liquids using pressure as an experimental variable because we realized that only by separating the effects of density and temperature on the molecular motions one can unravel the details of the dynamic structure of liquids and other disordered materials. Therefore, we developed unique NMR instrumentation which allowed us to carry out the NMR experiments on various disordered systems over a wide range of pressures and temperatures. There is currently no other laboratory in the U.S.A. and abroad with comparable performance features of the experimental NMR high pressure setup. Both high resolution NMR solution techniques and high resolution solid-state NMR techniques, including magic-angle-spinning and cross polarization are used in our laboratory. Second, our research group is the only one which used two powerful techniques - NMR and also laser Raman scattering on a specific material. Clearly, this approach results in a significant synergistic effect. We have recently started using infrared, static and dynamic light scattering, and small angle neutron scattering techniques in our studies of the sol-gel process. In order to fully exploit the NMR or Raman data our group also measures more mundane but necessary properties such as PVT, diffusion and shear viscosities. Third, we have adopted a systematic approach in our studies, which approach is a prerequisite for successful solution of the complex problem of liquids, gels, glasses and polymers. Fourth, our experiments are always conceived with a specific goal of either testing current theories or providing new results which serve as a basis for developing new theoretical models.

2. Research Accomplishments Under Grant AFOSR 89-0099

Since most of the accomplishments have already been discussed in interim reports, the presentation in this final report is limited to abstracts of key articles published during this grant period.

2.1 Molecular Level Understanding of the Sol-Gel Process

2.11 Effects of Various Amide Additives on the Tetramethoxysilane Sol-Gel Process

The effects of various amides, including formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide and N,N-dimethylacetamide, on the pore morphology of resulting xerogels prepared from tetramethoxysilane are studied by the BET pore analysis method. Shear viscosity and NMR line width measurements provide additional information about the effects of additives on the sol-gel process.

2.12 High Pressure ^{29}Si NMR Study of the Sol-Gel Process

^{29}Si -NMR spectroscopy is used to investigate the role of pressure on the hydrolysis and condensation kinetics of the tetramethoxysilane (TMOS) sol-gel process under neutral conditions. The time evolution of the concentrations of the various functional groups in a neutral solution has been monitored as a function of pressure from 40 bar to 460 bar. The concentration changes of TMOS and both the hydrolysis and condensation products are accelerated by pressure. The features of the time evolution of each species are very similar to each other between 40 to 460 bar by using t/t_{gel} as the time scale. Quantitative reaction rate constants for hydrolysis and condensation reactions are found for the early stage of the process; the latter ($0.91 \cdot 10^{-2}/\text{hrM}$) was higher than the former ($1.73 \cdot 10^{-4}/\text{hrM}$) at 1 bar. The observed activation volumes of these two reactions are determined as $-29 \text{ cm}^3/\text{mole}$ for hydrolysis and $-44 \text{ cm}^3/\text{mole}$ for condensation rate than on the hydrolysis rate. These ΔV^\ddagger values are discussed in terms of the intrinsic and solvation components of the activation volume based on the transition state theory. A comparison has been made to related data from sol-gel systems under other conditions.

2.2 Highly Viscous Liquids Including Lubricants

2.21 High Pressure NMR Study of Transport and Relaxation in Complex Liquids

The self-diffusion coefficients, densities, and shear viscosities of liquid 2-ethylhexylcyclohexanecarboxylate (EHC) were measured as a function of pressure from 1 to 4500 bar within the temperature range from -20 to 80°C . The Stokes-Einstein equation is applicable over 5 order of magnitude changes in self-diffusion and viscosity. The experimental data obtained are compared to those for the complex liquid of 2-ethylhexylbenzoate (EHB) in order to characterize the molecular structure effect of the replacement of the benzene ring with a saturated cyclohexyl ring. In particular, the low-temperature data suggest that conjugation of the phenyl ring with the ester group in EHB slows down diffusion and increases viscosity in comparison with EHC. Analysis in terms of the rough hard sphere model indicates a high degree of rotational-translational coupling which increases as density increases. By use of high-resolution, high-pressure NMR techniques the natural-abundance ^{13}C spin-lattice relaxation times, T_1 , and nuclear Overhauser enhancement were measured for each individual carbon in EHC and EHB over the same range of temperatures and pressures. An approximate analysis of the experimental T_1 data indicates anisotropic reorientation with multiple internal rotations.

2.22 High Pressure NMR Study of Carbon-13 Relaxation in 2-Ethylhexylbenzoate and 2-Ethylhexylcyclohexanoate

Natural abundance carbon-13 spin-lattice relaxation times and ^{13}C - ^1H nuclear Overhauser enhancement (NOE) times of 2-ethylhexylbenzoate (EHB) and 2-ethylhexylcyclohexanecarboxylate (EHC) have been measured along isotherms of -20, 0, 20, 40, and 80°C at pressures of 1-5000 bars using high-pressure, high-resolution NMR techniques. The ability to use pressure as an experimental variable has allowed us to study a wide range of molecular motions from extreme narrowing into the slow motional regime. In addition, the high-resolution capability even at high pressure permits the measurement of ^{13}C and NOE for each individual carbon in the molecules studied. Relaxation in both molecules is successfully analyzed in terms of a model assuming a Cole-Davidson distribution of correlation times. The comparison of parameters used in the model demonstrates the increased flexibility of the EHC ring over the EHB ring and also shows how the presence of the flexible ring contributes to the increased over-all mobility of the EHC molecule. The analysis of molecular reorientations in terms of activation volumes also indicates that EHB motion is highly restricted at low temperature.

2.3 Fluids in Confined Geometries

2.31 Confined Geometry Effects on Reorientational Dynamics of Molecular Liquids in Porous Silica Glasses

This work investigates the relative role of the pure geometrical confinement and the strength of the surface effect on the dynamics of liquids in porous silica glasses prepared by the sol-gel process. The deuteron NMR spin-lattice relaxation times T_1 of several molecular liquids in porous silica glasses are reported as function of pore size in the range from 18 to 143 Å over the temperature range from 260 to 310 K. Molecular liquids studied include strongly interacting polar liquids such as pyridine- d_5 , aniline- d_5 , and nitrobenzene- d_5 , whereas the saturated cyclic hydrocarbon liquids of cyclohexane- d_{12} and cis-decalin- d_{18} represent the weakly interacting liquids. In a first approximation, toluene- d_1 and dioxane- d_8 are chosen as examples of liquids with intermediate interactions with the silica surface. The experimental relaxation data are analyzed by using the two-state, fast-exchange model which is found to be valid for the strongly interacting liquids and liquids with intermediate interactions. In terms of this model, the viscosity of the surface layer for pyridine- d_5 is about 30 times higher than that for bulk liquid pyridine. The importance of the two-dimensional approach to describe motional dynamics of liquids confined to pores smaller than 30 Å is illustrated in the case of weakly interacting liquid of cyclohexane- d_{12} . Additional information on the relative role of surface interactions and the pure topological effects on the dynamics of liquids in confined geometries was obtained by using surface-modified glasses in which the surface hydroxyl groups were replaced by $\text{OSi}(\text{CH}_3)_2\text{OC}_2\text{H}_5$ groups. Indeed, the effects of surface modifications on the ^2H T_1 's are most pronounced for strongly interacting liquids whereas they are absent for cyclohexane. In agreement with the concept of two-dimensional behavior of liquids in small pores, one finds that the low-frequency relaxation times, namely, the spin-spin relaxation time T_2 , and the spin-lattice relaxation time in the rotating coordinate frame, $T_{1\rho}$, remain unchanged by surface modification. In fact, this is a consequence of logarithmic enhancement of the spectral density at low frequencies so that the effect of pure geometrical confinement on the T_2^{-1} and $T_{1\rho}^{-1}$ relaxation rates is much larger than any relaxation rate changes arising from surface modification. Several selected NMR T_1 experiments on pyridine- d_5 confined to anopore and zeolites are also presented.

2.32 Pressure Effects on Reorientational Dynamics of Molecular Liquids in Confined Geometries

In view of its fundamental and technological importance, it is not surprising to find that the problem of liquid behavior in confined geometries continues to attract attention. The present study represents a continuation of our efforts to improve the understanding of reorientational dynamics of molecular liquids confined to porous silica glasses prepared by the sol-gel process. So far, all NMR or other spectroscopic studies were performed at ambient pressure, and the present work demonstrates the feasibility of high pressure experiments on liquids confined to porous silica glasses. In particular, the finding of the applicability of the two-state, fast exchange model to analyze the NMR relaxation data provided the main motivation for the present high pressure experiments. The main goal of our experiments is to determine the effects of pressure on the dynamics of liquids in the surface layer by using the two-state, fast exchange model and compare to the behavior found for bulk liquids. The deuteron NMR spin-lattice relaxation times, T_1 , in liquid pyridine- d_5 were measured as a function of pressure up to 5 kbar at 300K in bulk liquid pyridine- d_5 and pyridine- d_5 confined to porous silica glasses with 18.4 Å, 24.1 Å, 32.8 Å and 69.4 Å pore radii.

3. Publications Supported by the Grant AFOSR 89-0099

"Solid State ^{29}Si and ^{11}B NMR Studies of Sol-Gel Derived Borosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, *J. Non-Cryst. Solids* **101**, 249-254 (1988).

" ^{27}Al and ^{29}Si NMR Study of Sol-Gel Derived Aluminosilicates and Sodium Aluminosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, *J. of Materials Science* **23**, 2908-2912 (1988).

"Self-Diffusion in Compressed, Highly Viscous Liquid 2-Ethylhexylbenzoate," N. A. Walker, D. M. Lamb, S. T. Adamy, J. Jonas and M. P. Dare-Edwards, *J. Phys. Chem.* **92**, 3675-3679 (1988).

"The Effect of Fluoride on the Sol-Gel Process," R. Winter, J.-B. Chan, R. Frattini and J. Jonas, *J. Non-Cryst. Solids* **105**, 214-222 (1988).

"The Structural and Dynamical Properties of the Sol-Gel Transition," R. Winter, D.-W. Hua, X. Song and J. Jonas, ILL Workshop, "Dynamics of Disordered Materials," Grenoble, France, September 1988.

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"Molecular Level Understanding of the Sol-Gel Process," Jiri Jonas, Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. J. D. Mackenzie and D. R. Ulrich (J. W. Wiley, NY), 1989.

"NMR and Raman Studies of FLuids," J. Jonas, 12th AIRAPT and 27th EHPRG International Conference on High Pressure Science and Technology, Paderborn, FRG, 1989.

"High Pressure 1D and 2D NMR Experiments on Model Biomembranes," R. Winter, P. Grandinetti, D. Driscoll and J. Jonas, 12th AIRAPT and 27th EHPRG International Conference on High Pressure Science and Technology, Paderborn, FRG, 1989.

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"NMR Studies of the Sol-Gel Process," J. Jonas, Proc. Ultrastructure Processing Conference, "Chemical Processing of Advanced Materials," Ed. Larry L. Hench and Jon K. West, (J. Wiley, NY) 1992, Chapter 9, pp. 93-101.

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Steven Taylor Adamy, "Nuclear Magnetic Resonance Studies of Highly Compressed Fluids" 1991

Duen-Wu Hua, "Experimental Study of Physical-Chemical Factors in the Sol-Gel Process" 1991

Jar-Bee Chan, "NMR Studies of the Chemical Additives Effect on the Sol-Gel Process" 1990

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COMPLETED PROJECT SUMMARY

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PUBLICATIONS:

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

An improved molecular level understanding of the fundamental relationship between molecular properties and macroscopic properties of highly viscous liquids and sol-gel prepared glasses represented the main goal of research supported by this grant. In addition, the behavior of fluids in confined geometries was investigated. Further development of unique NMR and laser Raman scattering instrumentation for experiments under extreme conditions of high pressure continued to represent an important part of our research.

In the project dealing with liquids confined to porous glasses, we succeeded, for the first time, to investigate the effect of pressure on the dynamics of liquids confined to porous glasses, and also to record a high-resolution NMR spectrum of a model lubricant in confined geometries. These unique experiments not only open new directions in the research on liquids in confined geometries but have important implications for the applied field of lubrication.